

LIQUID SMOKE: PRODUCT OF HARDWOOD PYROLYSIS

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Introduction

Liquid smoke compositions are obtained from pyrolysis of hardwood. These solutions are used to impart flavor, color, texture and in certain cases provide enhanced shelf life for food products. The constituents of liquid smoke are obtained from thermal degradation reactions of cellulose, hemicellulose and lignin. More than four hundred compounds have been detected in wood smoke.¹ In order to express the composition from an application stand point, the compounds in liquid smoke have been lumped together as three functional groups: carboxylic acids, phenols, and carbonyls. Cellulose and hemicellulose degradation are the primary sources of carbonyls and carboxylic acids, while phenols are obtained from lignin pyrolysis. In addition to these functional classes, there are other products like alcohols, lactones, and hydrocarbons.

The main variables that control liquid smoke product yield and characteristics are temperature, rate of heat transfer, particle size, atmosphere of pyrolysis, vapor and particle residence times, and composition of biomass. The developments related to control of these variables for improved product and process capabilities have resulted in several patents and publications over the last two decades in the field of liquid smoke. The difference in heat transfer rates results in different product yields. Rapid heat transfer rates are associated with fast pyrolysis systems.² Further liquid smoke flavors with different attributes can be made by varying the feedstock.³ Experiments were done in a bench scale reactor system under conditions of slow pyrolysis. The characteristics of liquid obtained from such bench scale experiments were compared with commercial product.

Experimental

Bench-scale Pyrolysis of Dried Saw-dust Under Atmospheric Conditions:³

Dried mixed hard wood saw-dust (150 gm, 8 % moisture) was weighed into a 4-inch diameter, 14 inch long laboratory size quartz rotary kiln and placed in a heated tube furnace. The reaction tube was rotated, so as to mimic the industrial process of a horizontal rotary kiln. The vapors from pyrolysis were then condensed in two vertical condensers in series. The first condenser was held at 65 °C and the second was held at 5 °C. The non-condensable vapors were then passed through filters for removing any aerosols, before being vented off. The liquids collected in the condensers were weighed. The test time was dependent on the time required for the char bed to attain the desired bed temperature. The test was stopped when gas evolution was not observed at the desired char bed temperature.

Analysis of Aqueous Condensate:³

The condensates were diluted with water, and analyzed for their overall composition for acid and phenol content.⁴ The procedures used for composition analysis were those used in the liquid smoke industry. The acid content was determined by titration and expressed as percentage acetic acid. The phenols were determined by colorimetric methods using 2,6-dimethoxy phenol (Aldrich Chemical Co., U.S.A) as standard.³ In this procedure liquid smoke solutions and standard solutions are complexed with 2,6-dichloroquinine-4-chloroimide (Aldrich Chemical Co. U.S.A) in a borate buffer solution at a pH of 8.3. The reaction is allowed to proceed for 30 minutes at room temperature. The color of the resulting complex is measured at 580

nm. The performance characteristics for the ability of carbonyls in liquid smoke to react with proteins was measured by staining index.³ This index is obtained by measuring the net absorbance of a reacted sample of glycine and liquid smoke at 440 nm in a glacial acetic acid solution.³

Results and Discussion

The product yields from bench scale experiments at various temperatures are presented in table 1.

Table 1. Hardwood Saw-dust Pyrolysis Product Yields from Bench scale Experiment:

Temperature °C	Liquid yield (%)	Char yield (%)
350	45.7	37.5
400	51.5	28.8
475	59.6	22.8
600	54.7	18.9

The yield values indicate an increase in liquefaction type reactions with increasing temperature. For similar temperatures, higher liquid and lower char yields are obtained from fast pyrolysis type process. The mechanisms involved in the degradation process of the saw dust components to various products have been presented by various researchers.^{4,5,6} The composition analysis of the aqueous fraction from bench scale experiments for liquid smoke type characteristics are presented in table 2.

Table 2. Composition Analysis (range) for Aqueous Fraction from Bench Scale Pyrolysis Experiments

Temperature range °C	400 –600°C
Acidity %	6.1 – 7.2
Phenol (mg/ml)	9.9 – 11.1
Stain index	69.6 – 81.5

The composition analysis indicates an increase in smoke components in the aqueous fraction with increase in temperature. In a traditional liquid smoke manufacture saw-dust is pyrolyzed in temperature ranges of 350-600°C, under atmospheric pressure conditions. The vapors from pyrolysis are condensed and contacted with water. The aqueous condensate is allowed to settle for a period of ten to fourteen days. During this period, an insoluble organic fraction referred to as tar separates out. This fraction carries with it particulates and PAH compounds that are generated and condensed during the manufacturing process. The benzo(a)pyrene content of the resulting aqueous smoke is less than 2ppb. PAH characterization of liquid smoke can be done by HPLC –fluorescence spectroscopy or GC-MS.⁷ A typical liquid smoke product from slow pyrolysis has the following average composition⁴: acidity =10.8%, phenol = 17.8 mg/ml, stain index =91.6. The acid and phenol concentration in liquid smoke indicate the flavor strength. The stain index value, provides information on the reactivity of the carbonyl compounds in liquid smoke towards non-enzymatic maillard type browning reactions with amino acids when applied on protein substrates. Thus it is observed that the aqueous extract from bench scale experiments have characteristics similar to a commercial liquid smoke product.

Conclusion:

The similarities in compositional analysis data from bench scale experiments and commercial product indicate suitability of the bench scale experiments to study biomass pyrolysis chemistry for liquid smoke manufacture. Liquid smoke, a product of the biomass pyrolysis provides a safe alternative to food processors over conventional smoke houses. The clean up steps used in the manufacturing process makes it a safe ingredient.

References:

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